

Studies into sub 100 nm resists for Proton Beam Writing.

JA van Kan¹ AA Bettoli¹, T. Osipowicz² and F Watt³

¹Assistant Prof physics department and Engineering Science programme, NUS

²Deputy Director of CIBA and professor in the physics department of NUS,

³Director of CIBA and professor in the physics department of NUS.

Centre for Ion Beam Applications (CIBA) Physics department, Faculty of Science, National University of Singapore (NUS), 2 Science Drive 3 Singapore 117542

Web <http://www.ciba.nus.edu.sg>

I Aim of the project

Investigations into the characteristics of HSQ a new high resolution resists for p-beam writing, investigations into other potential resists for proton beam writing. Optimizing proton beam focusing through adjusted secondary electron detection. Develop computer models to simulate the interactions of the proton beam and resist below the 100 nm level to study proximity effects in proton beam writing.

II Scientific achievements

Our project AOARD 06-4004 has resulted in 5 scientific publications in the area of resist investigation for proton beam writing [1,2,3], optimized proton beam focusing through new methods of detecting secondary electrons [4] and theoretical calculations which show the absence of proximity effects in proton beam writing [5]. Main achievement: paper in nano letters in which HSQ is introduced as a superior resist for proton beam writing down to the 20 nm level [1].

In 2006-2007 we have also published 3 papers related to our AOARD 05-4037 project, one focused on the fabrication of microlenses [6] a second one on the optimized fabrication of resolution standards for proton beam writing [7]. A third paper discusses the use of proton beam writing for the fabrication of metal stencil masks for LIGA X-ray fabrication [8].

In 2006-2007 I have conducted 9 guest lectures and conference seminars on proton beam writing.

- 1 **Massachusetts Institute of Technology, Boston, USA, 2006.**
- 2 Charged Particle Optics Group, Faculty of Applied Sciences, Delft University of Technology, the Netherlands, 2007.
- 3 Physics department, Bristol University, UK, 2007.
- 4 CAFI-NEODE, Neuchatel, Switzerland, 2007.
- 5 Air Force Office of Scientific Research, Washington DC, USA, 2006, supported by the US air force through a WOS grant.
- 6 **Invited review talk: 2006** at the International Conference on Nuclear Microprobe Technology and applications / Second international Proton beam writing workshop (Singapore)
- 7 **Invited oral presentation** at NanoBiz Meet 2007, Singapore.
- 8 Oral presentation: 2007 7th High Aspect Ratio Microstructure Technology conference (Besancon, France).
- 9 Oral presentation: 2006 at the Materials Research Society Spring meeting, San Francisco.

In 2007 both Andrew Bettoli and Jeroen van Kan got promoted to assistant professor.

2007 OMICRON Prize for nano technology

In 2007 Jeroen van Kan has received the Omicron prize for his work on innovative nano technology research performed in Singapore. A large part of his work has been made possible through the support from the US air force under grant numbers: AOARD 04-4021, AOARD 05-4037 and AOARD 06-4004.

Report Documentation Page			<i>Form Approved OMB No. 0704-0188</i>	
<p>Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p>				
1. REPORT DATE 05 JUL 2007	2. REPORT TYPE Final	3. DATES COVERED 31-05-2006 to 30-05-2007		
4. TITLE AND SUBTITLE Studies into sub 100 nm resists for Proton Beam Writing.		5a. CONTRACT NUMBER FA48690610031	5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	5d. PROJECT NUMBER	
6. AUTHOR(S) Jeroen van Kan		5e. TASK NUMBER	5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Research Center for Nuclear Microscopy, Dept of Physics, National Univ, of Singapore, Lower Kent Ridge Road, Singapore 119260, SP, 119260		8. PERFORMING ORGANIZATION REPORT NUMBER N/A		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AOARD, UNIT 45002, APO, AP, 96337-5002		10. SPONSOR/MONITOR'S ACRONYM(S) AOARD		
		11. SPONSOR/MONITOR'S REPORT NUMBER(S) AOARD-064004		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT Our project AOARD 06-4004 has resulted in 5 scientific publications in the area of resist investigation for proton beam writing, optimized proton beam focusing through new methods of detecting secondary electrons and theoretical calculations which show the absence of proximity effects in proton beam writing. Main achievement: paper in nano letters in which HSQ is introduced as a superior resist for proton beam writing down to the 20 nm level. In 2006-2007 we have also published 3 papers related to our AOARD 05-4037 project, one focused on the fabrication of microlenses a second one on the optimized fabrication of resolution standards for proton beam writing. A third paper discusses the use of proton beam writing for the fabrication of metal stencil masks for LIGA X-ray fabrication.				
15. SUBJECT TERMS nanodevices, proton micromachining				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 6
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified	19a. NAME OF RESPONSIBLE PERSON	

Resist investigations for proton beam writing

Three different resists have been investigated for their effectiveness in combination with PBW. Prior to the work described here the only compatible resists which have demonstrated sub-100 nm features are PMMA and SU-8. In this project, we have demonstrated that hydrogen silsesquioxane (HSQ) resist is a powerful non C based resist for PBW. The results obtained with PBW using the HSQ resist, show that HSQ behaves as a negative resist under proton beam exposure [1]. Details down to the 22 nm in width standing at a height of 850 nm have been directly written in HSQ see fig. 1. The superior resolution of HSQ shows great potential but unlike PMMA and SU-8 this resist has a limited shelf life. To optimize the usage of this resist contrast curves and sensitivity of HSQ as a function of shelf life have been measured [2], see fig. 2. We found that timing in HSQ resist processing is a critical factor in achieving nm sized features.

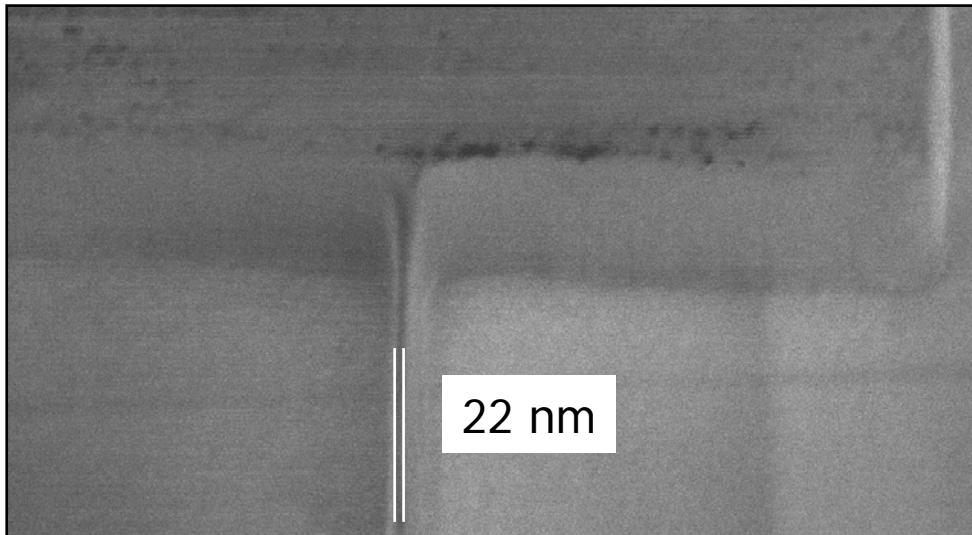


Fig 1 SEM images of a 22 nm wide line written with a 2 MeV H_2^+ beam in 850 nm thick HSQ

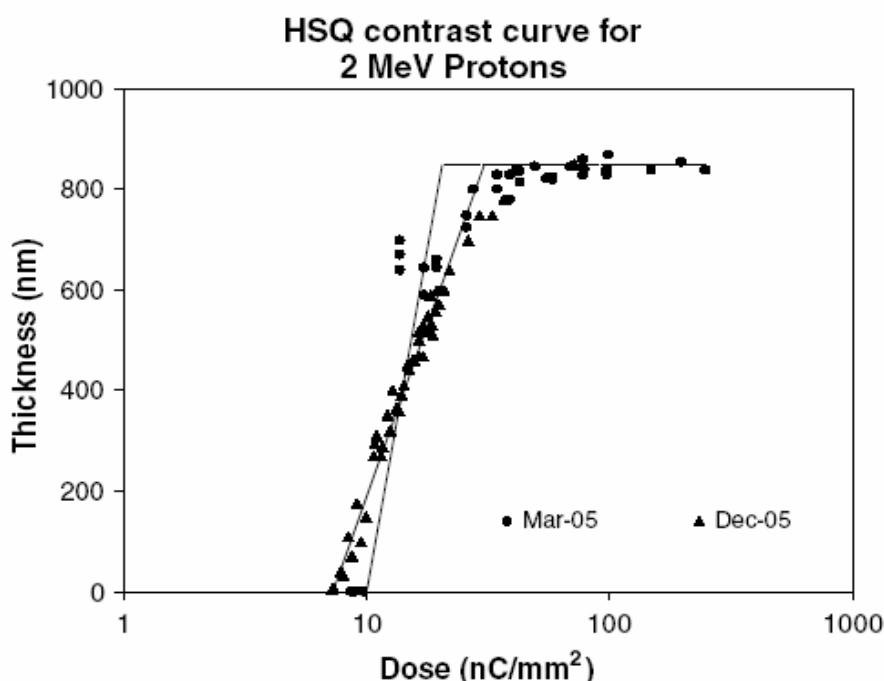


Fig 2 Contrast curve for 850 nm thick HSQ, exposed to 2MeV protons, the straight lines correspond to a contrast of 3.2 and 1.7 for the fresh and 10 month old resist, respectively.

The second resist is a spin-coatable TiO_2 resist for which sub 10 nm resolution has been reported using electron beam writing. In PBW smooth side walls have been observed for this resist, see fig. 3. Despite a relative low sensitivity of this resist for PBW (8000 nC/mm²) it has potential applications in the area of integrated optical components such as waveguides and gratings because of its high refractive index [3]. Further optimization is required to reduce the stress in the resist to avoid cracking of the resist during the drying of the resist after spincoating.

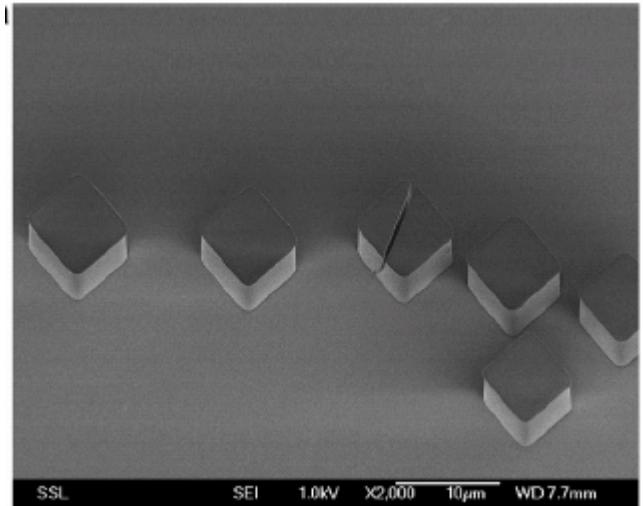


Fig. 3 SEM photo of $5 \times 5 \mu m^2$ squares in TiO , written with 1MeV protons applying a dose ranging from 10,000 up to 50,000 nC/mm².

Finally WL-7154 a UV-sensitive negative resist has been evaluated in collaboration with Dow Corning. It shows high sensitivity for PBW (4 nC/mm²). The first results show it is possible to write details below a micron in this resist, see fig 4. This resist could function as a mold for Ni electroplating to fabricate Ni stamps for nanoimprint- and soft-lithography [3].

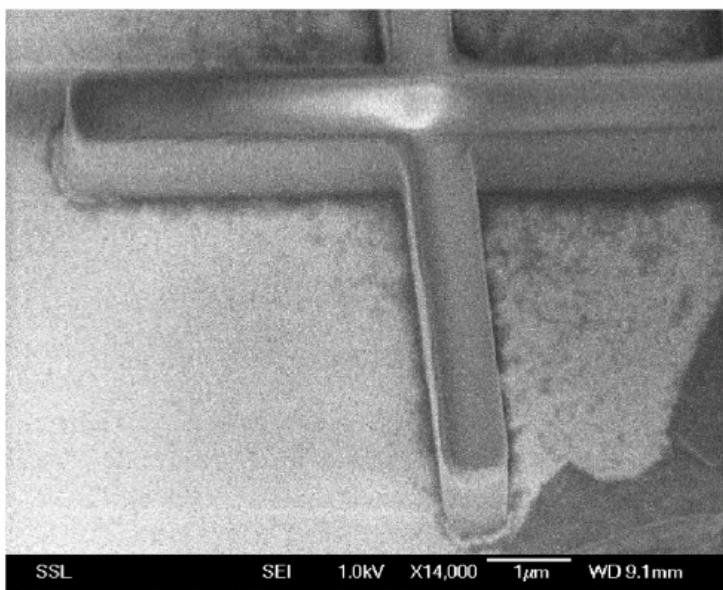


Fig. 4. SEM photo of sub-micron lines written in a $1.4 \mu m$ thick layer of WL-7154 using a 2 MeV proton beam focused down to $300 \times 300 \text{ nm}^2$.

Optimized secondary electron imaging with protons

To make PBW more user-friendly it is important to have a fast way to focus the proton beam to small spot sizes. To quantify the focus of the proton beam a high resolution grid is imaged. The conventional mode of imaging used up to now has utilized conventional nuclear microprobe

signals that are of a pulsed nature and are inherently slow. In this work, we report the new imaging system that has been introduced, which uses proton induced secondary electrons. This in conjunction with software developed in-house that uses a National Instruments DAQ card with hardware triggering, facilitates large data transfer rates enabling rapid imaging. Frame rates as much as 10 frames/s have been achieved at an imaging resolution of 512 x 512 pixels. The electron imaging system is based on attracting the electrons from the target. The system includes a cage and biasing ring, they are at positive potentials, attached to a glass tube. The cage first attracts the secondary electrons from the target which are then accelerated by the ring to impinge on a P-47 powder scintillator. The generated luminescence is then coupled via the quartz tube to a photomultiplier tube whose output current is amplified and converted into a voltage. Our imaging/scanning hardware uses these signals to generate fast high quality secondary electron images of our resolution standard. An example of a high resolution image of a Ni resolution standard is shown in fig. 5 (left) and compared with a conventional Rutherford backscatter image of the Ni grid (right) [4].

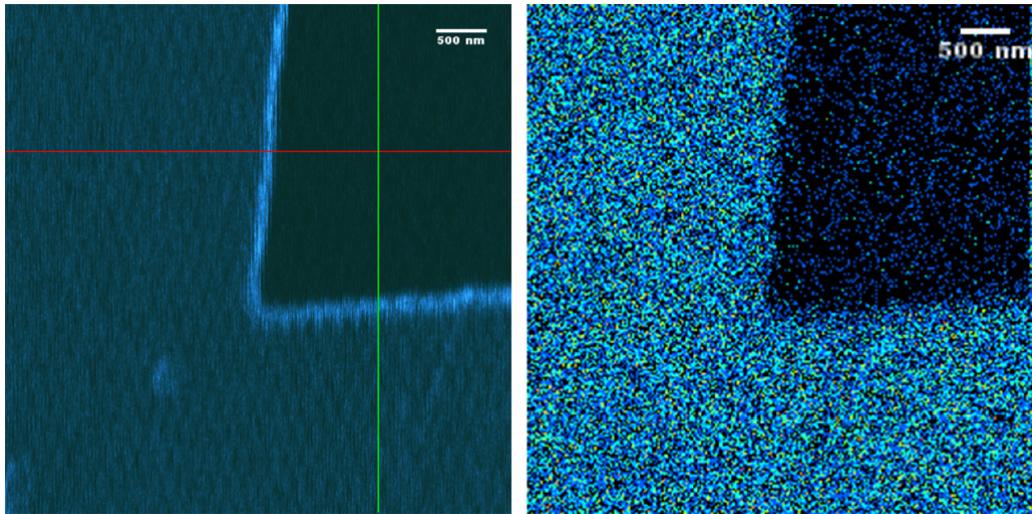


Fig. 5 Proton induced secondary electron image (left) and a conventional Rutherford back scatter image of a Ni grid resolution standard.

Calculations of proximity effects in proton beam writing

The generation of secondary electrons (or δ -rays) represents a significant mode of energy loss and energy delocalisation in the penetration of a charged particle into matter. Owing to the large mass disparity between electrons and protons, the trajectories of penetrating protons are essentially straight while those of electrons are tortuous and the fractional energy transferred to secondary electrons by individual protons are much less than with electrons. This suggests that protons are fundamentally capable of exhibiting superior proximity effects over electrons when used in lithography, no supporting evidence has yet been presented. In the present study we utilise the Hansen–Kocbach–Stolterfoht model for proton induced secondary electron emission to develop a Monte Carlo model capable of recreating the energy deposition profiles resulting from the creation and propagation of δ -rays produced by the passage of MeV protons in PMMA. In Fig 6 it is shown that after traveling 2 μm through a PMMA layer the energy deposited by a 2 MeV proton beam is well maintained within a radius of 10 nm whereas a 20 keV electron beam has completely spread over an area of more than 1 μm^2 . We show that protons possess more confined energy deposition profiles than electrons. The simulation results presented in [5] are indicative of the superior nature of p-beam writing over e-beam writing with respect to the extent of proximity effects. The use of protons for lithography can result in more confined energy profiles while also permitting structures of high aspect ratios.

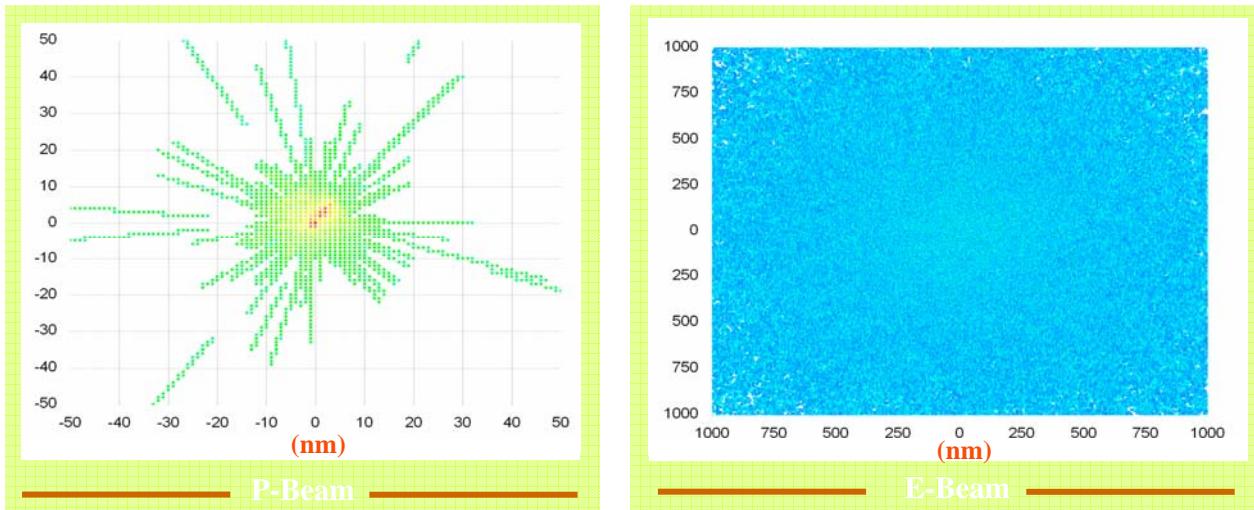


Fig 6 Energy deposition caused by generated δ -rays for a focused 2 MeV proton beam (left) and a focused 20 keV electron beam after traveling through 2 μm of PMMA resist.

Summary

We have introduced HSQ as new high resolution resist for proton beam writing. Structures down to the 20 nm level have been written in HSQ, standing at a height of 850nm. WL-7154 and TiO_2 resist have been evaluated. They don't have extreme resolution but could be used in areas like mold fabrication and specific optical applications respectively. A new fast electron detection system has been introduced which allows the fast and accurate focusing of MeV protons. Finally we have shown theoretically through Monte Carlo simulations that the proximity effects in proton beam writing are far superior compared with electron beam writing.

Dr. Jeroen A. Van Kan
 Assistant professor
 Centre for Ion Beam Applications (CIBA)
 Engineering Science Programme and Department of Physics,
 The National University of Singapore
 2 Science Drive 3
 Singapore 117542
 Tel: (65) 68742638, (65) 68742639(lab)
 Fax: : (65)67776126
 E-mail: phyjavk@nus.edu.sg
 Web <http://www.CIBA.nus.edu.sg>

References

- 1 Proton Beam Writing of Three-Dimensional Nanostructures in Hydrogen Silsesquioxane, Jeroen A. van Kan, Andrew A. Bettoli, and Frank Watt, *Nano Letters*, Vol 6 No. 3, (2006) 579-582
- 2 Hydrogen silsesquioxane a next generation resist for proton beam writing at the 20 nm level, J.A. van Kan, A.A. Bettoli and F. Watt, *Nuclear Instruments & Methods in Physics Research Section B*-Volume 260 (2007) 396-399.
- 3 New resists for proton beam writing, J.A. van Kan, A.A. Bettoli, S.Y. Chiam, M.S.M. Saifullah, K.R.V. Subramanian, M.E. Welland and F. Watt, *Nuclear Instruments & Methods in Physics Research Section B*-Volume 260 (2007) 460-463.
- 4 The rapid secondary electron imaging system of the proton beam writer at CIBA, C.N.B. Udalagama, A.A. Bettoli, J.A. van Kan, E.J. Teo and F. Watt, *Nuclear Instruments & Methods in Physics Research Section B*-Volume 260 (2007) 390-395.
- 5 A Monte Carlo study of the extent of proximity effects in e-beam and p-beam writing of PMMA C.N.B. Udalagama, A.A. Bettoli, F. Watt, *Nuclear Instruments & Methods in Physics Research Section B*-Volume 260 (2007) 384-389
- 6 Polymer microlens replication by Nanoimprint Lithography using proton beam fabricated Ni stamp, R.K. Dutta, J.A. van Kan, A.A. Bettoli and F. Watt, *Nuclear Instruments & Methods in Physics Research Section B*-Volume 260 (2007) 464-467.
- 7 Fabrication of free standing resolution standards using proton beam writing, F. Zhang, J.A. van Kan, S.Y. Chiam and F. Watt, *Nuclear Instruments & Methods in Physics Research Section B*-Volume 260 (2007) 474-478.
- 8 Proton beam writing: a tool for high-aspect ratio mask production, J.A. van Kan, P.G. Shao, K. Ansari, A.A. Bettoli, T. Osipowicz and F. Watt, *Microsystem Technologies Microsystem Technologies*, V13 Issue 5-6 (2007) 431-434